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LASER-INDUCED FLUORESCENCE LINE NARROWING
OF Eu^{3+} IN LITHIUM BORATE GLASS

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Abstract

Laser-induced fluorescence line narrowing reveals structural changes in Eu^{3+} doped borate glasses as a function of Li_2O network modifier concentration. These changes are discussed in terms of different coordination and bonding and possible phase separation.

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Laser-induced fluorescence line narrowing has recently been used to investigate the local environment and interactions of paramagnetic ions in glass. Since the resulting spectra are sensitive to structural modifications, this technique has been applied to simple alkali borate glasses (1,2) where the relative numbers of network-forming BO_3 triangles and BO_4 tetrahedra (3) and the existence of subliquidus immiscibility (4,5) are dependent upon the mole fraction of alkali oxide.

Paramagnetic ions generally enter a glass as interstitial network-modifying cations, not as substitutional ions. Because of differences in the bonding to near neighbours the local fields at individual ion sites vary, resulting in large inhomogeneous linewidths in absorption and emission. In the past, analysis of structure arising from changes in borate glass composition was hampered by the simultaneous observation of many sites. This difficulty can be overcome by the use of a narrowband laser source (6). In our studies trivalent europium is used as the probe ion because it has a relatively simple energy level scheme.

Previous investigations (1,2) of lithium borate glasses revealed large differences in the FLN spectra of Eu^{3+} for samples containing 10 and 40 mole percent of Li_2O . Whereas the spectra from the two samples were similar for laser excitation on the low energy side of an inhomogeneously broadened band, at high excitation energies additional lines appeared in the spectra from the 10 mole % Li_2O glass. Among the possible causes of this behaviour is phase separation into, say, a lithia-rich and a borate-rich phase. To examine the possibility further, we have investigated glasses with smaller Li_2O contents approaching the case of simple B_2O_3 .

Details of the glass preparation procedure and of the experimental techniques used are outlined in Ref. 1. In the case of glass preparation,

attempts to make clear Eu_2O_3 -doped B_2O_3 glasses failed; glasses with concentrations as low as 0.01 mol.% Eu_2O_3 and 99.99 mol.% B_2O_3 , though clear at elevated temperatures in the melt, would change color on cooling indicating a type of phase separation. Li_2O was added until a clear glass was formed with 0.1 mol.% Eu_2O_3 and the remainder B_2O_3 . The lowest concentration of Li_2O that would form a clear glass on cooling was 3 mol.%.

The laser-induced FLN spectra from the $^5\text{D}_0$ state of Eu^{3+} to the $^7\text{F}_1$ and $^7\text{F}_2$ manifolds are shown in Fig. 1 for 3 and 40 mol.% Li_2O borate samples. The laser excitation energy (cm^{-1}) is given at the left of each spectrum (the spectra are not normalized to constant excitation energy). The fluorescence spectra in Fig. 1 show some line narrowing, but the widths are still greater than either the homogeneous or instrumentation widths because the spectra were recorded with nonresonant excitation.

The change in line positions in the FLN spectra with excitation energy arise from differences in the local fields. As first reported by Motegi and Shionoya,⁷ the variation in crystal-field splitting exhibits a monotonic change with $^7\text{F}_0$ - $^5\text{D}_0$ excitation energy. The low-energy excitation portions of the FLN spectra for the two samples are very similar suggesting that they arise from Eu^{3+} ions having equal coordination and bonding. The high-energy excitation portions, however, are very different. In addition, extra lines appear in the 3% Li_2O sample which are identical to those observed previously in a 10% Li_2O sample¹ and which are attributed to Eu^{3+} ions in sites having a different local environment. These lines are labeled 3, 4 and 7 in Fig. 1.

The fields at Eu^{3+} sites are expected to change as Li_2O content is

increased because boron with three coordinating oxygens is replaced by boron with four coordinating oxygens and by Li^+ network modifying cations. An increase in the Eu-O covalency reduces the Racah parameters which, in turn, lowers the $^5\text{D}-^7\text{F}$ energy separation. A similar effect has been observed for Nd^{3+} in $x\text{Li}_2\text{O} (1-x)\text{B}_2\text{O}_3$ glasses(8) where the $^4\text{I}-^4\text{F}$ separation decreases with increasing Li_2O content for $0 < x \leq 0.45$. This is already apparent from the shift of the peak at the strong $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ fluorescence band at 300 K. Therefore, in the case of Eu^{3+} the low energy side of the inhomogeneous $^7\text{F}_0-^5\text{D}_0$ transition corresponds to sites with stronger Eu-O interaction and covalency. Conversely, one would expect that the high-excitation-energy spectra should arise from sites where BO_3 triangles are prevalent. At 40% Li_2O concentration, where the maximum number of BO_3 triangles are converted into BO_4 tetrahedra, one would expect to see evidence of Eu^{3+} in sites of both coordinations. The spectra, however, vary monotonically with pump energy and do not exhibit any dramatic change at high pump energies. In addition, the lifetimes of all of the luminescence lines at any one pump wavelength are identical in this sample indicating that one type of coordination is predominant. In the 3 and 10% samples, the additional lines appearing at high pump energies have lifetimes different from those of the regular lines so that two types of sites are being simultaneously pumped.

Metastable immiscibility on a scale of 5-500 nm is known to occur in the lithium borate system.^{4,5} Lithium-rich and B_2O_3 -rich phases are expected to be present in the 10% Li_2O sample since the maximum of the coexistence curve occurs at this concentration. If impurities such as Eu^{3+} enter one or both phases, the excitation energies may be sufficiently different to permit

relative probing of local structure in the individual phases. If two phases are present in the 10% Li_2O sample, the low-energy FLN spectra suggest that one phase is similar to that of the 40% Li_2O sample. On the basis of the nephelauxetic effect, such a phase is likely to be the Li_2O -rich phase, where the concentration of BO_4 tetrahedra may be of the same order as in the 40% sample. Further support for this theory is found in samples of lower Li_2O concentration. The 3% Li_2O sample behaves identically to the 10% sample but it is noteworthy that for a Li_2O concentration of 3% the maximum Eu doping possible is only 0.2%. Consequently, at such concentrations the relative numbers of Eu ions and Li ions present are roughly similar to those of the 10% sample.

Europium ions cannot be introduced into simple B_2O_3 glass in the absence of Li_2O . The network of $(\text{BO}_3)^3$ units in glassy B_2O_3 is tightly bonded by bridging oxygens. Trivalent Eu ions cannot enter this network substitutionally (because of size), nor, apparently, as a network modifier. If, however, a network modifier such as Li^+ is present, it disrupts the network and non-bridging oxygens occur. In the vicinity of the looser structure, Eu^{3+} may be incorporated as modifier ions.

Additional spectral lines could also arise from clustering of Eu^{3+} ions on a Eu^{3+} rich phase. If ion-ion interactions are strong, they can alter the energy levels from those for isolated Eu^{3+} ions.

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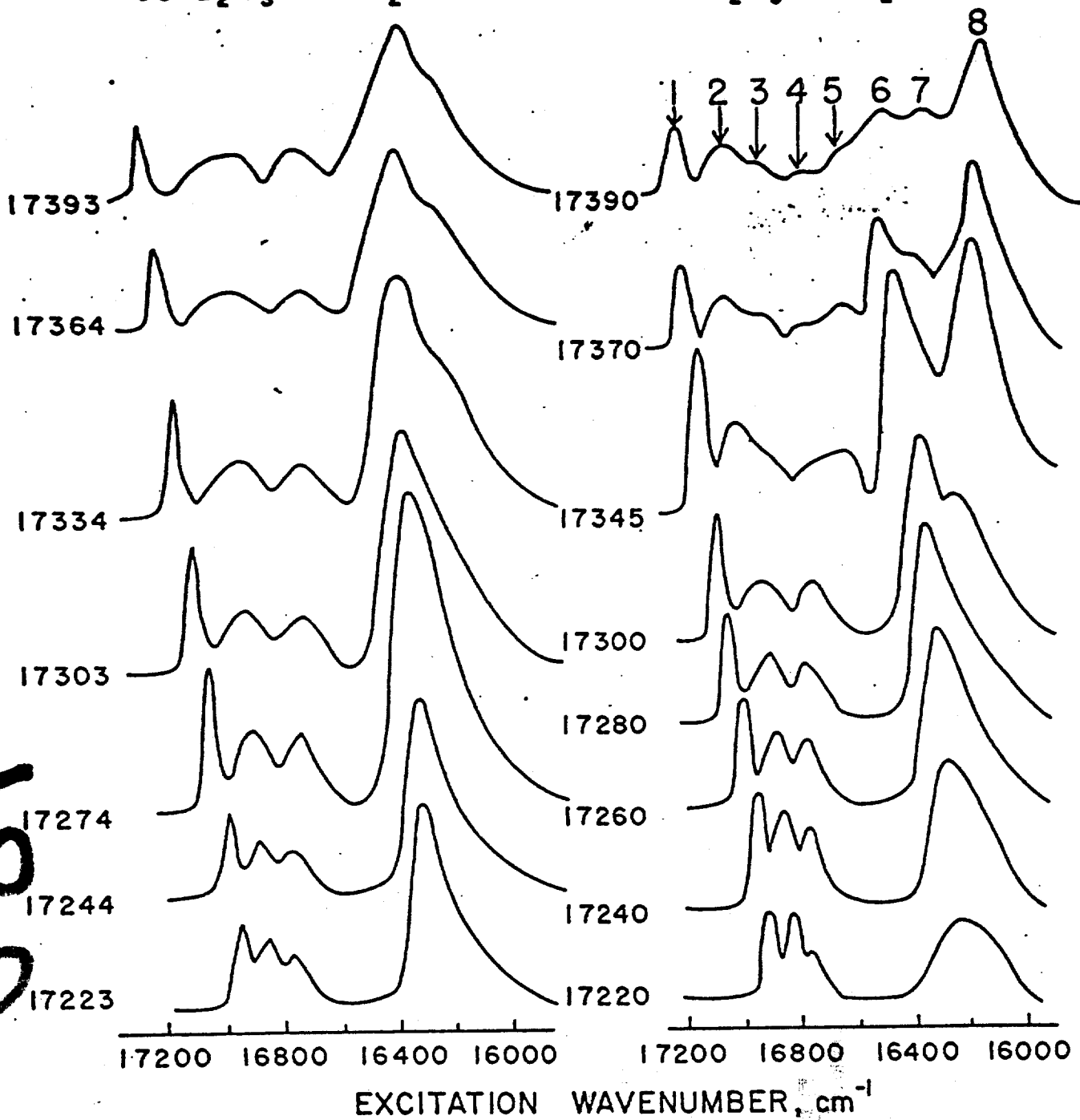
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Figure Captions

Fig. 1. Comparison of the ${}^5\text{D}_0 - {}^7\text{F}_1$, ${}^7\text{F}_2$ fluorescence spectra of Eu^{3+} in $3 \text{ Li}_2\text{O} \cdot 97 \text{ B}_2\text{O}_3$ and $40 \text{ Li}_2\text{O} \cdot 60 \text{ B}_2\text{O}_3$ glasses at 1.7K as a function of ${}^7\text{F}_0 - {}^5\text{D}_0$ excitation frequency (cm^{-1}).

60 B₂O₃ · 40 Li₂O

97 B₂O₃ · 3 Li₂O



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